Determination of antiferromagnetic interactions in Zn(Mn)O, Zn(Co)O, and Zn(Mn)Te by inelastic neutron scattering

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The nearest-neighbor magnetic exchange interactions in $Zn_{0.95}Mn_{0.05}O$, $Zn_{0.95}Co_{0.05}O$, and $Zn_{0.98}Mn_{0.02}Te$ were investigated by measuring inelastic neutron scattering from isolated exchange-coupled spin-spin pairs. The experiments on $Zn_{0.98}Mn_{0.02}Te$ were carried out at atmospheric pressure and then at 4 kbar pressure in order to determine the dependence of the exchange parameter on the spin-spin distance. © *2006 American Institute of Physics*.
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One of the central issues in ongoing magnetic semiconductor research is the question of "how to make these materials ferromagnetic."[1] As found from the experiment and theoretical studies,[2,3] a particularly efficient mechanism leading to ferromagnetic (FM) states is hole-assisted exchange between substitutional magnetic ions embedded in semiconducting crystal lattices. Ferromagnetism produced by this mechanism is observed, e.g., in strongly *p*-type $Ga_{1-x}Mn_xAs$ (Ref. 1 and $Zn_{1-x}Mn_xTe$.[4,5] According to theoretical predictions, strongly *p*-type alloys of $Zn_{1-x}Mn_xO$ and $Zn_{1-x}Co_xO$ have the potential to remain FM even at room temperature. Therefore, much effort has been recently focused on investigating these two latter systems. However, it should be kept in mind that in such alloys there are also intrinsic antiferromagnetic (AFM) interactions arising from a superexchange mechanism. In order to obtain a FM material, the carrier-induced FM component has to prevail over the intrinsic AFM interactions. Hence, good knowledge of these latter interactions is certainly important for working out the "best strategy" of making the systems ferromagnetic.

In view of the above, we have performed inelastic neutron scattering experiments in order to determine the nearest-neighbor (NN) AFM exchange parameter J_1 in diluted samples of $Zn_{1-x}Mn_xO$ and $Zn_{1-x}Co_xO$. Specifically, scattering from isolated spin-spin pairs was investigated. This method enables one to directly determine the pair excitation energies, and thus to obtain highly accurate values of the exchange parameters.[6] It has been used in the past to measure the NN exchange parameters between substitutional Mn and Co ions in ZnS, ZnSe, and ZnTe,[5,7] but no such studies have yet been done for the ZnO-based systems.

However, further studies of ZnS-, ZnSe-, and ZnTe-based alloys are also worth pursuing because they may lead to better understanding of the intrinsic AFM interactions in the entire family of alloys derived from the II-VI compounds. In particular, experimental information about the change of J with varying spin-spin distance may help to improve the existing theoretical models.[8,9] Such data can be obtained from inelastic neutron scattering experiments at high pressures. In order to test the feasibility of this method, we performed "pilot" high pressure experiments on $Zn_{1-x}Mn_xTe$.

The simplest form of the exchange Hamiltonian for a spin pair is

$$\mathcal{H}_{ij} = -2J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j. \tag{1}$$

In addition to NN pairs, there are also singlets, triplets, and higher order configurations. In magnetic semiconductors derived from the II-VI compounds (i.e., of the $A^{II}_{1-x}\mathbf{T}_xB^{VI}$ composition, where $\mathbf{T}=\mathrm{Mn},\mathrm{Co},\ldots$), which are all of the zinc-blende or wurtzite structure, the probability that a given spin is a singlet (no magnetic NNs) is $P_1(x)=(1-x)$,[10] that it belongs to a pair is $P_2(x)=12x(1-x)$[18], and so on. Thus for a sample with $x=0.05$, 54% of the magnetic spins are singlets, 24% form doublets, 4% triplets, and the remaining end up in higher order formations.[11]

The dominant feature being probed is that of magnetic pairs randomly distributed and oriented in the material. The technique is not sensitive to spin singlets, which are the most common formation; the triplets and higher order formations are more rare in occurrence, thus contributing little to the signal and are of sufficiently different energy to not interfere with peak positions obtained from magnetic pairs. An isolated spin pair of Mn^{2+} ions (each having $S=\frac{5}{2}$) with interactions described by Eq. (1) has energy eigenvalues $E(S_T=S_T(S_T+1)|J_{ij}|$, where S_T is the total spin of the pair

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which takes the values $S_T=0,1,2\ldots,5$. Transitions are limited to adjacent energy levels and may be stimulated through inelastic neutron scattering.[6] This results in a neutron energy gain/loss equal to the transition energy, which follows $\Delta E = \pm 2|J_{ij}|, \pm 4|J_{ij}|, \ldots, \pm 10|J_{ij}|$.

Measurements were performed at the NIST Center for Neutron Research (NCNR) (Gaithersburg, MD, USA) using the disk-chopper time-of-flight spectrometer (DCS TOF). Using an array of nearly 1000 He-3 detectors positioned to collect data over a wide Q-range, the DCS TOF is an excellent high-luminosity instrument for studying dispersionless dynamic modes (which is the case in localized excitations of spin clusters). Also, the instrument has good energy resolution in the ΔE range required for these experiments. Measurements were performed predominately at a neutron energy of 3.55 meV corresponding to a wavelength of 4.8 Å. Some runs were also made at lower energy, 1.67 meV or 7.0 Å, for increased resolution, though the tradeoff for this is a substantial decrease in the scattered intensity.

For the experiments 7 g polycrystalline samples of $Zn_{0.95}Mn_{0.05}O$ and $Zn_{0.95}Co_{0.05}O$ were used. The specimens were prepared by high-temperature sintering.[10] During the measurements the samples were kept at a temperature of 120 K after being mounted in a Displex refrigerator.

The $Zn_{0.98}Mn_{0.02}Te$ sample was grown in a single-crystal form using the Bridgeman method. Approximately 1 cm^3 of the crystal was powdered and placed into the pressure vessel, a cylindrical aluminum cell designed for high pressure work. The cell was cooled to 40 K using a helium cryostat. An unpressurized run was made to provide the base line data. The cell was then pressured using helium gas to 400 MPa (4 kbars) and another run was performed to measure the shift in J_1 due to the shortened spin-spin distance.

The high pressure data from the $Zn_{0.98}Mn_{0.02}Te$ sample seems very promising for future experimentation regarding variations in exchange interaction strength with respect to spin-spin distance. The atmospheric pressure measurement yielded distinct peaks corresponding to the $|1\rangle \rightarrow |0\rangle$ and $|2\rangle \rightarrow |1\rangle$ transitions (the numbers in the "kets" represent the total spin S_T in a given quantum state of the pair). The observed peak positions agreed very well with the results of earlier experiments on a much larger specimen from the same batch performed on a different instrument.[5] At high pressure (4 kbars), the peaks shifted to higher energies. A comparison of the $|2\rangle \rightarrow |1\rangle$ peaks seen at atmospheric and high pressure is shown in Fig. 1. The fitted peak positions are 3.18 ± 0.03 and 3.338 ± 0.03 meV, respectively. This yields the two different exchange constants $J_1^{\mathrm{atm}}=-0.795$ meV and $J_1^{\mathrm{press}}=-0.836$ meV.

The DCS instrument enables simultaneous observation of inelastic scattering and Bragg reflections from polycrystalline samples. The shift of the (111) reflection observed at 4 kbars corresponds to NN distance decrease of 0.49%. As shown by our data, such a shortening leads to a 5% increase of $|J_1|$.

The two ZnO-based systems were studied only at atmospheric pressure. The inelastic peak pattern seen in the $Zn_{0.95}Mn_{0.05}O$ spectrum (Fig. 2) appears to be more complicated than the simple $\Delta E=2|J_1|,4|J_1|,6|J_1|,\ldots$ sequence corresponding to a single J_1 value. The data clearly points to *two different* J_1 values: one of them gives rise to the three peaks seen at Fig. 2 at −3.047, −6.017, and −8.798 meV positions, and the other to the two peaks centered at −4.045 and −8.027 meV. An explanation for that can be readily given, considering that $Zn_{1-x}Mn_xO$ is of wurtzite structure. In contrast to the situation in $Zn_{1-x}Mn_xTe$ and other zinc-blende (cubic) systems, in the hexagonal wurtzite arrangement all NN pairs are not strictly symmetry equivalent. Arguably, one of the observed spectrum component represents the exchange constant J_1^{in} for "in-plane" NN spins [i.e., both are located in the same (0001)-type plane], and another the J_1^{out} constant for "out-of-plane" NNs [i.e., those located in adjacent (0001)-type planes]. Such a splitting in the NN interaction has been observed before in magnetization step spectroscopy (MSS) studies of two other wurtzite structure diluted magnetic semiconductor (DMS) materials, $Cd_{1-x}Mn_xS$ and $Cd_{1-x}Mn_xSe$.[12] However, there is no way as of yet to determine from the experimental results which peaks correspond to the in-plane and out-of-plane exchange interactions.

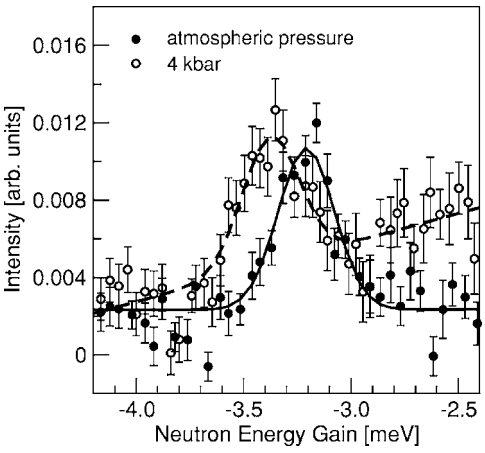

FIG. 1. Inelastic peaks from $Zn_{0.98}Mn_{0.02}Te$ corresponding to the $|2\rangle \rightarrow |1\rangle$ transition on NN spin pairs, at atmospheric pressure and at 4 kbars. The fitted maximum energy values are -3.18 ± 0.03 and -3.338 ± 0.03 meV, respectively. The negative sign of the energy transfer represents the crystal energy loss.

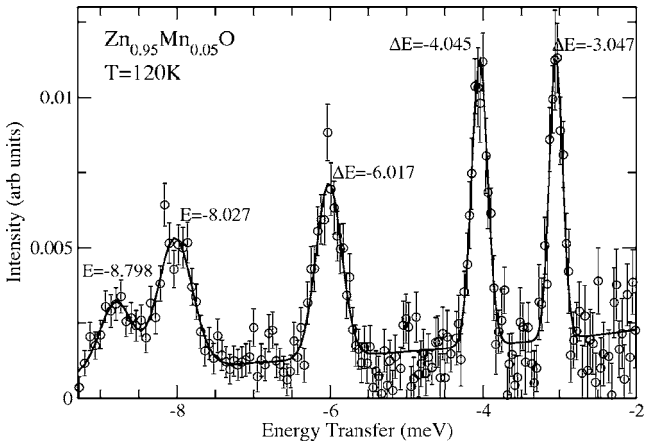

FIG. 2. Inelastic scattering spectrum from $Zn_{0.95}Mn_{0.05}O$ at 120 K, showing several maxima corresponding to transitions between energy levels of NN spin pairs.

In ideal wurtzite arrangement the lattice has a ratio of $c/a=\sqrt{8/3}=1.633$ and all NNs are equidistant; however, in all wurtzite type II-VI DMS systems the lattices are "squished" in the out of plane direction yielding lower c/a values. This leads to an asymmetry in which the out-of-plane NNs are closer than the in-plane ones. In particular, in $Zn_{1-x}Mn_xO$ where $c/a=1.601$,[10] these distances differ by 1.29%. Such a large difference would suggests that the larger of the two exchange parameters observed represents the out-of-plane interactions. On the other hand, it has also been theorized that even in a perfect lattice the J_1^{in} and J_1^{out} strengths would differ due to the different symmetries of the in-plane and out-of-plane NNs. The dominant superexchange pathway is the same for both groups, however, different secondary pathways are available. As predicted by Larson,[13] due to that difference $|J_1^{in}|$ should not be smaller, but *larger* than $|J_1^{out}|$ by as much as 16%.

In addition to the splitting phenomenon, the peaks do not seem to be following the initially supposed progression of $\Delta E=2|J|,4|J|,6|J|,\ldots$ very well as it quickly begins "overshooting" the peaks. However, as shown in Ref. 14, such a deviation is caused by higher-order terms in the Heisenberg interactions. When a correction is made in the form of a second order biquadratic term in the exchange Hamiltonian,

$$\mathcal{H}_{ij}=-2J\mathbf{S}_i\cdot\mathbf{S}_j-4K(\mathbf{S}_i\cdot\mathbf{S}_j)^2, \tag{2}$$

which yields the following energy levels: $E(S_T)=-JS_T(S_T+1)-KS_T^2(S_T+1)^2-4KS_T(S_T+1)S(S+1)$. This provides the following peak progression: $\Delta E=-2J+66K,-4J+108K,-6J+102K,\ldots$, which indeed fits the data obtained from the $Zn_{0.95}Mn_{0.05}O$ system quite well. With the progression fit to the data, values of J_1 and K_1 were obtained: $J_1'=-1.38\pm0.02$ and $K_1'=0.0044\pm0.0007$ meV for the first progression and $J_1''=-1.89\pm0.03$ and $K_1''=0.004\pm0.001$ meV for the second. This represents a large change; a shift of 36% from J' to J'', though it is as yet impossible to determine which belongs to the in-plane or out-of-plane interactions due to the opposing effects of the closer NN in the out-of-plane pairs and the greater superexchange between in-plane pairs. More work both theoretical and experimental must be done before these values may be assigned to a lattice orientation.

It should be mentioned that the value of J_1 inferred from recent magnetic susceptibility studies of $Zn_{1-x}Mn_xO$ (Ref. 10) is 1.18 ± 0.06 meV.

Experiments on $Zn_{0.95}Co_{0.05}O$ have not yielded fully conclusive results. The results of earlier studies[7,12] indicate that in II-VI DMSs the Co–Co interactions are three to four times stronger than the Mn–Mn ones. In the ΔE range covered by our measurements ($\sim$16 meV wide) only a single peak was seen at $\Delta E=-13$ meV that could be attributed to scattering from NN Co–Co pairs. Hopefully future experiments using higher neutron incident energy will reveal more spectrum details.

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